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THE MODIFIED CHEMICAL CONSTITUENT OF SEA WATER INTRUDING INTO THE COASTAL AQUIFER

By

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Abstract

Intruding sea water into the aquifer often has different chemical composition from that of original sea water. Such phenomena are observed in the coastal region of Beppu Spä and explained by the process of cation exchange between intruding sea water and soil being in contact with thermal water for a long time before salt contamination. As the result, mixing sea water becomes rich in Ca ion and poor in Na ion in the period of initial stage of sea water intrusion, but recovers to the original sea water with progress of intrusion.

Concentrations of iodine in intruding sea water are found to be much larger than those in the ocean from the observations in Beppu and Obama Späs. However, ratios of Br/Cl or I/Cl in thermal water containing large salt concentrations are found to be usefull as the index of contamination by the sea water.

1. Introduction

We have often found relatively large concentrations of salts in deep groundwater, especially in thermal waters. Their source waters are classified, from a view-point of the origin of chlorine, as magmatic, connate or intruding sea water, but the definite conditions to divide them were not cleared until now in spite of many chemical investigations.

It is well-known that influent sea water to the inland aquifer cannot maintain its original chemical composition which is almost universally constant in the ocean. Then, processes of chemical modification of sea water passing through soils are considered to be very important not only for the recognition of mixing sea water but for the hydrological research to evaluate the proceeding path of sea water intrusion. It seems possible that those processes will be more clearly observed in the coastal thermal water region than in the usual cold groundwater aquifer for thermal groundwater contains relatively large concentration of salt of different constituent from sea water. It is then considered most usefull for this problem to investigate the thermal water

samples from coastal spä, where progress of sea water intrusion has been ascertained by other various researches.

A part of Beppu Spä has been suffered by salt contaminations of thermal water. Kikkawa and Karube (1950) reported that this was owing to the infiltration of sea water with the drawdown of the piezometric heads of the thermal groundwater.

Chemical analyses were carried out for the water samples collected from 54 drill-holes in this region in July 1963. Positions of drill-holes and distribution of chlorine contents are shown in Fig. 1. The depths of drill-holes in this area range from 66 to 150 meters and almost of all are discharged by pumps. Chlorine contents vary in relatively large range, the highest of which reaches to about 11 g/l. We assume that the area of sea water intrusion is limited by the isochlorine of 500 mg/l shown as A-B curve in Fig. 1, since the distribution of Cl' contents shows sharply diminishing gradient from the inland side of the isochlorine curve of 1 g/l to the low content of 2~300 mg/l being usual value in Beppu City, though Cl' contents larger than 500 mg/l widely vary in this coastal area.

2. Area of sea water intrusion in Beppu

Chemical analyses of thermal water in this area was first carried out by I. Yamashita and others in 1926. Their result (1937) indicates that the area of large salt concentrations (Cl' 1~6 g/l) was limited only in the southern part,

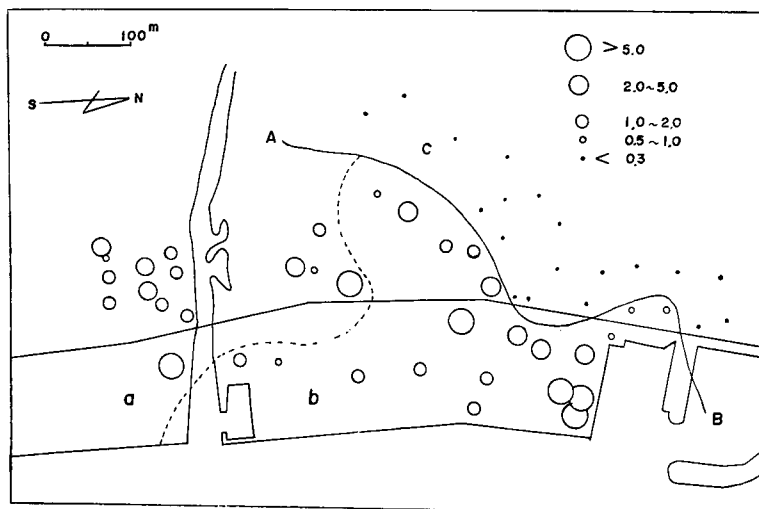


Fig. 1. Positions of observed bore-holes and distribution of Cl' content. (g/l)
A-B curve indicates the limit of sea water intrusion.

named as Hamawaki, and that in other part, named as Beppu, Cl' contents were almost in the range of 2~300 mg/l. Kikkawa and Karube (1950) reported that the area of large Cl' content extended northward towards the present sea water intrusion area as in Fig. 1. After that, the progress of intrusion area has not been appeared in spite of several times observations. Then, it can be said that the sea water intrusion had progressed in about ten years after 1937 from region a to regions a and b when we divide the present intrusion area into two regions, a and b, by dotted line in Fig. 1. Region a is named Hamawaki and b is Beppu. The area of inland side of A-B curve is named as region c where mixing of sea water is assumed to be not occurred. All of above-mentioned data in sea water intrusion area show that the relations between Cl' and other chief ions of thermal water are similar to that of sea water except excess of Ca ion and lack of Na ion which are common to almost all samples.

There were eight samples in region b in 1937. All of them have similar compositions to the present samples in region c which are taken as original thermal water before mixing of sea water. Mean values of their concentrations represented by meq/l are listed in Table 1 and the percentages of each ion to total anion or cation are compared with sea water.

Table 1. Comparison between chemical compositions of thermal water and sea water.

| | | Cl | SO_4 | HCO_3 | Na | Mg | Ca | K |
|---------------|-------|-------|---------------|----------------|-------|------|------|-----|
| Thermal water | meq/l | 4.5 | 1.2 | 6.5 | 5.4 | 2.7 | 3.2 | 0.4 |
| | % | 36.9 | 9.8 | 53.2 | 48.2 | 22.1 | 26.3 | 3.2 |
| Sea water | % | 90.3 | 9.3 | 0.4 | 77.4 | 17.6 | 3.4 | 1.6 |
| Difference | % | -33.4 | 0.5 | 52.8 | -29.4 | 4.8 | 22.9 | 1.6 |

3. Cation exchange

As chlorine is known unchangeable in nature, we compare the contents of each ion to Cl' for each sample. Among them, relations to Ca^{++} and Na^+ are presented in Figs. 2 and 3 which show quite interesting informations for modifications in chemical composition of sea water. Each value from analysis in 1963 is plotted as circle for region a and black point for region b. Dotted lines indicate the relations when thermal water as listed in Table 1 mixes the sea water by various ratios. Considerable differences are appeared between relations for samples from regions a and b. The formers distribute nearly along the dotted line but the latters cannot be explained only by the mixing of sea water. It is especially interesting that concentrations of Ca ion are so large that some of them are nearly equal to the maximum value calculated

from solubility product of $[\text{CaSO}_4]$ to sea water. Diminishes of Na ion are also distinctly.

Considering that concentrations of SO_4 ion in these samples are rather small compared with those calculated from the assumption of simple mixing of sea water and that thermal water before sea water intrusion in this region has poor concentration of Ca ion (about 60 mg/l), we cannot presume the existence of soluble calcium strata under the ground in this area. When the values in region a from analysis in 1926 are also plotted as cross marks in Figs. 2 and 3, it is noted that they give similar distribution to that of region b in 1963, apart from that of region a in the present.

Such results tell us that the chemical composition of sea water intruding into region a before 1926 had passed through the process making rich in Ca and poor in Na, but after that, it recovered to the original composition in the ocean with the progress of intruding area to the neighborhood region b where the process of modifying chemical character of intruding sea water still continued until now. Then, it is probable to presume that the mechanism changing chemical character of sea water actively influences in the period of initial

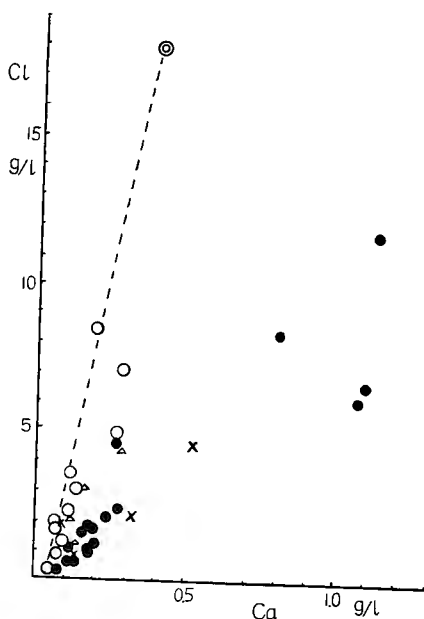


Fig. 2. Relation between contents of Cl^- and Ca^{++} .

- Samples from region a in 1963
- Samples from region b in 1963
- × Samples from region a in 1926
- △ Samples from region a in 1946

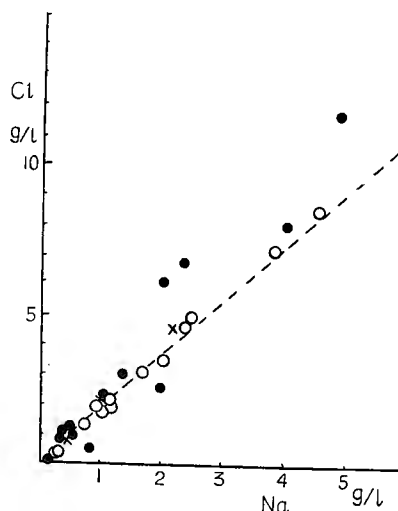


Fig. 3. Relation between contents of Cl^- and Na^+ .

stage of influx through the aquifer and gradually diminishes with progress of intrusion. Such mechanism may be performed by cation exchange between sea water and soil in the aquifer.

From a view-point of equivalent ratios of each cation to total cation, thermal water percolating through the aquifer before sea water intrusion has exceedingly larger value to Ca ion and smaller to Na ion than sea water as mentioned in Table 1. When we assume that the chemical nature of soil in the aquifer was in equilibrium with that of thermal water before salt contamination, intrusion of sea water would break that equilibrium and begin to change chemical composition of percolating sea water so as to establish the new equilibrium between soil and moving water through the aquifer. Accordingly, intruding sea water gradually modifies its chemical character in accordance with the path of hydrological movement. From a view-point of chemical composition, sea water mixing to thermal water in the aquifer is not original sea water but is to be called as modified sea water. The ability of cation exchange of soil is diminished with time after soil particles become in contact with new intruding sea water. Assuming such a process, it must be observed that composition of cations contained in modified sea water would be close to original thermal water near the front of sea water intrusion and become to recover to that of original sea water in the region discharging salt mixing water for a long time.

We can calculate the chemical compositions of the mixing modified sea water from the result of chemical analysis for water samples in 1963, assuming that the concentration of Cl ion is not changed in the aquifer, and then, determine the equivalent ratio of each cation to total cation for each modified sea water at the position of observed bore-hole.

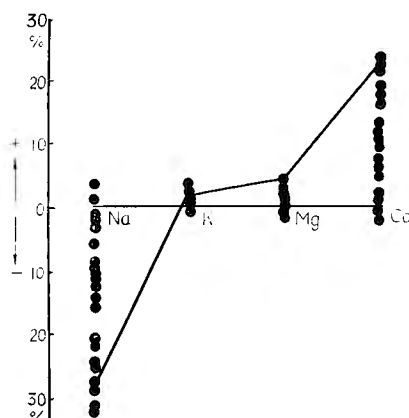


Fig. 4. Discrepancies of cation contents in modified sea water.

Fig. 4 shows the discrepancies between the ratios thus obtained and those of original sea water for each cation. Horizontal line means no discrepancies and oblique lines show discrepancies for imaginary water having the same chemical composition of cations as original thermal water indicated in Table 1. Positions of black points show gains in positive direction and losses in negative direction for modified sea water passing through the aquifer. It is easily understood from this figure that the modifications of chemical compositions of intruding sea water take place almost in the range between horizontal and oblique lines as expected from above-mentioned process of cation exchange to the soil being equilibrium with original thermal water for a long time before intrusion.

In the next, we try to obtain the geographical distribution of chemical character of modified sea water. As the variations of K and Mg ions are found to be negligibly small compared with those of Ca and Na ions from Fig. 4, it is probable that gains of Ca ion are nearly equal to losses of Na ion for modified sea waters. Equivalent ratios of Na ion to total cation of modified sea waters are calculated by above-mentioned method and their distribution is represented by isovalue curves in Fig. 5.

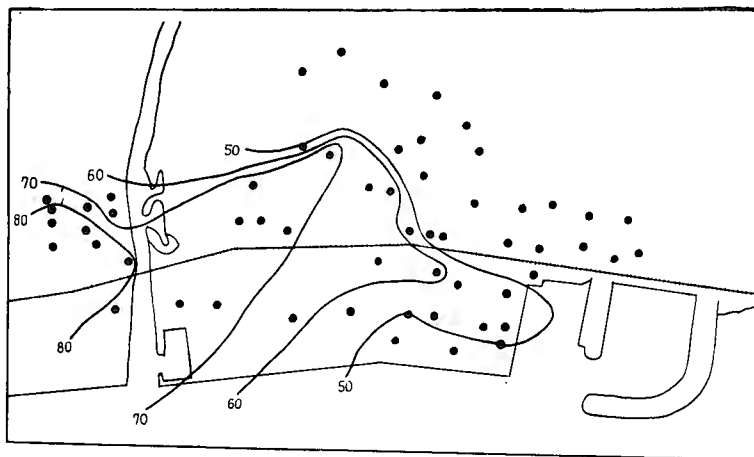


Fig. 5. Distribution of ratios of Na^+ to total cation (%) in the mixing sea water.

It is interesting to note that values of Na^+ content decreases northward in area of sea water intrusion and they have no relation with the concentration of Cl^- in water samples from bore-holes. This figure is well explained by the process of cation exchange between soil and sea water, considering that sea water intrusion has progressed through the path along the similar direction as diminishing of Na^+ content. It is probable to understand that soil in region

a has already attained to equilibrium state with original sea water by continuous influx of sea water and now no exchange take place in this region, but, on the contrary, that soil near the front of sea water intrusion still maintains its old character being in contact with original thermal water and constituents of mixing sea water are modified approximately to that of thermal water as expressed in Table 1.

Then, it may be concluded that the main cause making various chemical compositions of mixing sea water is the mutual action between soil particles and percolating sea water through the aquifer. Accordingly, the process of changing the composition of modified sea water will continue as long as the nature of soil in the salt-contaminating aquifer does not attain to equilibrium with that of original sea water.

It is considered to be an important future problem to investigate variations in the hydrological character of the aquifer in accompany with change of chemical character of soil.

4. Relations between contents of Bromine, Iodine and Chlorine

Some researchers published that the relations between concentrations of halogen are usefull to investigate the source of thermal water. For example, Nakamura and Maeda (1958) classified the sources of thermal water of large salt concentration using values of Br/Cl as follows.

- (1) Value of Br/Cl is about 3.4×10^{-3}mixing of sea water.
- (2) Value of Br/Cl is considerablly larger than 3.4×10^{-3}
.....mixing of connate water.
- (3) Value of Br/Cl ranges between 1 and 2.5×10^{-3}
.....mixing of magmatic water.

The ratio of I/Cl is also often used for the same purpose as the concentration of iodine in the ocean is much smaller than that in usual thermal water. It is well-known that the ratio of I/Cl is about 2.6×10^{-6} for the sea water near Japan but is $1 \sim 10 \times 10^{-4}$ in thermal water or volcanic gas.

However, it is considered necessary to research more quantitatively for abilities of preservation of such halogens in order to use their concentrations for the critical indices. Then, we determine the concentrations of bromine and iodine of the water samples from Beppu Spä as mentioned in previous section and compare them with Cl' contents. Simillar treatments are also performed for samples collected by authors in 1964 from Shirahama and Obama Späs, where sea water intrusions in recent times were ascertained by other observations.

All of the results are shown in Figs. 6, 7 and 8 with values obtained for

several boiling springs situated in hilly region in Beppu which contain large concentrations of Cl' . As contents of Br and Cl ions show almost positive linear relation, only the relation of Br/Cl and Cl' is illustrated in Fig. 6 in order to show variations of Br/Cl with mixing of sea water.

These figures tell us the behaviors of halogens with the progress of sea water intrusion.

(1) The values of Br/Cl approximate to 3.4×10^{-3} of original sea water when Cl' contents in thermal water become over 2 g/l. However we cannot decide only by the ratio of Br/Cl for water samples of smaller Cl' content than 1 g/l whether they are collected from boiling spring or from the area of sea water intrusion.

(2) It is noted that concentrations of iodine and chlorine show approximately positive linear relations both in Beppu and Obama. When these relations

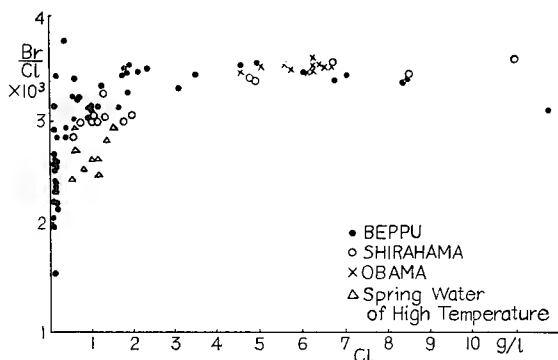


Fig. 6. Relation between Cl' and Br/Cl .

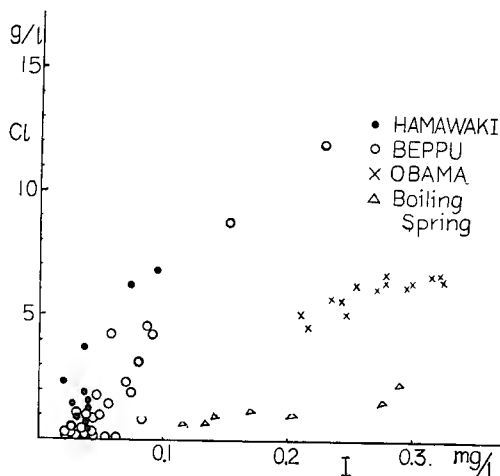
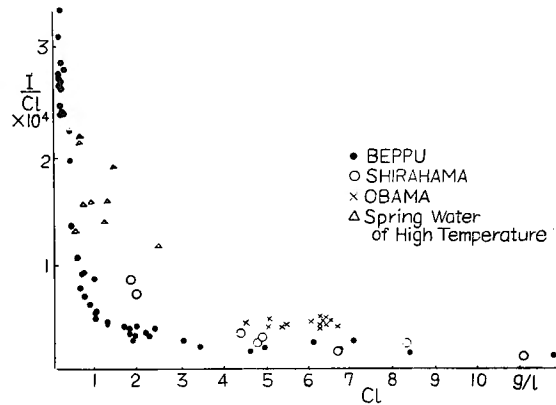


Fig. 7. Relation between contents of Cl and I ions.

Fig. 8. Relation between Cl' and I/Cl .

are assumed owing to simple mixing of original thermal water and the sea water, concentration of iodine in sea water must be about 0.35 mg/l in Beppu and much larger in Obama. On the contrary, concentration of iodine in sea water is considered in general as 0.05 mg/l and our result for the water sample collected from the sea about 1 km apart from the coast of Beppu shows the same value. However, the concentrations for sea water samples collected near the beach are 0.11 mg/l in average. Sea water intruding into the inland aquifer must contain about three times larger concentration of iodine than that in the sea near the beach. We cannot ascertain such sources of iodine, though it is expected that organic matter may give some effects through the path of sea water in intrusion.

However, it is probable to say that the gradient of linear relation between iodine and chlorine contents is much smaller than that of boiling springs or connate waters investigated until now.

In Shirahama Spä, such increases of iodine in intruding sea water are not found and it appears that iodine contents become smaller in accompany with increases of Cl' contents.

Then, it is probably expressed that, although concentration of iodine is not preserved through the process of sea water intrusion, the values of I/Cl in thermal water contaminated by intruding sea water are so small compared with those of boiling springs that it is useful to compare those values for investigating the source of thermal water. Researches on contents of halogens in thermal water are now continued by the authors.

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